

Non-Abelian Berry transport, spin coherent states, and Majorana points.

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Abstract

We consider the adiabatic evolution of Kramers degenerate pairs of spin states in a half-integer spin molecular magnet as the molecule is slowly rotated. To reveal the full details the of the quantum evolution, we use Majorana's parametrisation of a general state in the $2j + 1$ dimensional Hilbert space in terms of $2j$ Majorana points. We show that the intricate motion of the Majorana points may be described by a classical hamiltonian which is of the same form, but of quite different origin, as that which appears in the spin-coherent-state path integral. As an illustration we consider molecular magnets of the $j = 9/2$ Mn4 family and compute the frequency with which the magnetization varies. This frequency is generally different from the frequency of the rotation.

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I. INTRODUCTION

The controlled and measurable manipulation of quantum spin states is the basis of NMR with its abundance of practical applications. Another system in which spins may be manipulated and measured is provided by molecular magnets [1]. These materials consist of large organic molecules containing clusters of transition elements such as Mn or Fe, whose unpaired electron spins lock together to form a single large ($j \sim 10$) spin. The best known examples are Mn12, Fe8, and Mn4, for which $j = 10, 10$ and $9/2$ respectively. (The nomenclature focusses on the magnetic atoms. Mn12, for example, is shorthand for the polyacetate $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}\cdot(\text{H}_2\text{O})_4$.) The organic ligands surrounding the magnetic cluster serve to reduce the interaction between clusters so that each molecular spin behaves almost independently — yet, when the molecules have a common orientation and all experience the same external forces, the total magnetic moment is the sum of many identical molecular moments and so the spin direction may be observed. The energy of the spin \mathbf{J} depends on its orientation with respect to the host molecule, and one may think of the tip of the spin arrow as moving on a sphere through a potential landscape possessing hills, valleys and saddlepoints. This potential landscape can be manipulated by applying an external magnetic field. In Fe8, for example, the rate of quantum spin tunneling between eigenstates located in separate potential wells has been measured *via* the Landau-Zener crossing of the levels as the external field is varied [2].

An alternative route to manipulating the spin is simply to rotate the system. In most cases the magnetization will merely co-rotate with the molecule, but when the spin ground-state is degenerate we have more interesting possibilities. If the rotation is slow compared to the separation of the degenerate ground state from the first excited state, the evolution will be described by non-abelian Berry transport [3, 4]. Now a doubly-degenerate ground state is guaranteed by Kramers' theorem whenever the total spin is a half integer, and the Hamiltonian $H(\mathbf{J})$ governing the large spin's interaction with the host molecule is invariant under time reversal [5]. The aim of this paper is to explore how these Kramers-degenerate pairs evolve as a general anisotropic molecule is rotated.

When dealing with the $2j + 1$ dimensional Hilbert space of a large spin, the expectation $\langle\psi|\mathbf{J}|\psi\rangle$ reveals only a small part of the quantum information encoded in the spin state $|\psi\rangle$. A useful tool [6] for visualizing the complete quantum state is provided by the location of

the zeros on the unit sphere of the spin-coherent-state wavefunction $\psi(z)$. These zeros are the antipodes of “Majorana points” that can be thought of the directions of a set of $2j$ spin-1/2’s that compose the spin- j .

In section II we will review Majorana’s parametrisation [7] of a general spin- j state and explain its connection with spin-coherent state wavefunctions. In section III we will derive expressions for the non-abelian Berry connection one-form in terms of the Majorana parametrisation, and show how they simplify when we restrict to Kramers degenerate pairs of states. In sections IV and V we introduce an alternative way of thinking about the adiabatic Berry transport for Kramers pairs, and how the evolution of the state is described by a classical hamiltonian dynamical system. In the last section VI we show how even simple anisotropies can give rise to intricate state evolutions as a molecule is rotated, and that this intricacy may have experimentally observable consequences. In particular we will see that a steady period T rotation of the molecule can give rise to motions of the spin direction that are again periodic, but with a period that typically differs from T .

II. MAJORANA PARAMETRISATION AND SPIN COHERENT STATES

It is a familiar fact that when a collection of $2j$ spin-1/2 particles are combined into a single quantum system the spin- j representation of $SU(2)$ resides in the space of totally symmetric tensors. Elements of a symmetric tensor space $\text{Sym}[V^{\otimes r}]$ are sums of the form

$$A^{i_1 i_2 \dots i_r} \mathbf{e}_{i_1} \odot \mathbf{e}_{i_2} \odot \dots \odot \mathbf{e}_{i_r}, \quad (1)$$

where the \mathbf{e}_i are the basis vectors for V , and the symmetric tensor product “ \odot ” is defined to commutative and distributive:

$$\mathbf{a} \odot \mathbf{b} = \mathbf{b} \odot \mathbf{a}, \quad \mathbf{a} \odot (\lambda \mathbf{b} + \mu \mathbf{c}) = \lambda (\mathbf{a} \odot \mathbf{b}) + \mu (\mathbf{a} \odot \mathbf{c}). \quad (2)$$

In [7] Majorana showed that an arbitrary spin- j state $\Psi \in \text{Sym}[V_{1/2}^{\otimes 2j}]$ can be decomposed as

$$\Psi = \psi_{i_1} \odot \dots \odot \psi_{i_{2j}}, \quad (3)$$

where the

$$\psi_i = \alpha_i \mathbf{e}_1 + \beta_i \mathbf{e}_2 \quad (4)$$

are a set of $2j$ spin-1/2 spinors with $\mathbf{e}_1 \equiv |\uparrow\rangle$, $\mathbf{e}_2 = |\downarrow\rangle$. This result is perhaps surprising. Most elements of a general tensor product space (whether symmetric or not) cannot be decomposed into a single product; they can only be expressed as a *sums* of products. Majorana's result was rediscovered by Schwinger [8] and by Rabi [9], and later reviewed by Bloch and Rabi [10]. Schwinger's paper is historically interesting as in his equation (9) he draws attention to a previously omitted term in the equations describing the evolution of a spin in a time-varying field. This term is now recognizable as the "Berry Phase." Majorana's original paper is similarly notable in that it contains an independent derivation of the non-adiabatic level-crossing probability that is traditionally attributed to Landau, Stuckelberg and Zener.

Majorana's recipe for his decomposition is as follows: Given a spin- j state

$$\Psi \equiv |\Psi\rangle = \sum_m |j, m\rangle \langle j, m | \Psi \rangle \quad (5)$$

we construct a set of $2j + 1$ coefficients

$$c_{j-m} = \langle j, m | \Psi \rangle \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}}, \quad m = -j, -j+1, \dots, j-1, j \quad (6)$$

and the degree $2j$ polynomial equation

$$P_\Psi(z) = \sum_{n=0}^{2j} z^{2j-n} c_n = 0. \quad (7)$$

If the $2j$ roots of this polynomial are denoted by z_i , then the z_i are related to the coefficients of the spin-1/2 factors by

$$z_i = -\beta_i / \alpha_i. \quad (8)$$

We can extract the individual coefficients from their ratios by normalizing so that $|\alpha_i|^2 + |\beta_i|^2 = 1$, but a choice of phase remains for each ψ_i . These phases can be swapped amongst the factors leaving only an overall phase to be matched with that of Ψ .

It may happen that one or more of the leading coefficients c_n are zero. The polynomial equation then has degree less than $2j$ and possesses fewer than $2j$ roots. In this case it is convenient to extend the complex plane to the Riemann sphere, and regard the missing roots as being at infinity. Their corresponding α_i are then zero.

To understand why the recipe works, we use the commuting property of the symmetric tensor factors to allow the shorthand

$$\underbrace{\mathbf{e}_1 \odot \cdots \odot \mathbf{e}_1}_{j+m \text{ factors}} \odot \underbrace{\mathbf{e}_2 \odot \cdots \odot \mathbf{e}_2}_{j-m \text{ factors}} = \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m}. \quad (9)$$

To connect an expansion in terms of the $\mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m}$ with the more conventional expansion

$$\Psi \equiv |\Psi\rangle = \sum_m |j, m\rangle \langle j, m| \Psi\rangle \quad (10)$$

we need to define an inner product on the symmetric tensor-product space. The one that is induced naturally from the spin-1/2 product sets

$$\langle \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m} | \mathbf{e}_1^{j+m'} \mathbf{e}_2^{j-m'} \rangle = \delta_{mm'} \frac{(j+m)!(j-m)!}{(2j)!}. \quad (11)$$

From this we identify

$$|j, m\rangle = \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m}. \quad (12)$$

This natural inner product arises from regarding the symmetric tensor products as being symmetrized conventional tensor products. For example,

$$\mathbf{e}_1 \odot \mathbf{e}_1 \odot \mathbf{e}_2 \equiv \frac{1}{3} (\mathbf{e}_1 \otimes \mathbf{e}_1 \otimes \mathbf{e}_2 + \mathbf{e}_1 \otimes \mathbf{e}_2 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_1 \otimes \mathbf{e}_1). \quad (13)$$

In the general case, the 3 is replaced by

$$N_{jm} = \frac{(2j)!}{(j+m)!(j-m)!}, \quad (14)$$

which is the number of distinct terms generated when we symmetrize

$$\mathbf{e}_{i_1} \odot \mathbf{e}_{i_2} \odot \cdots \odot \mathbf{e}_{i_{2j}} = \frac{1}{(2j)!} \sum_{\pi \in \mathfrak{S}_{2j}} \mathbf{e}_{i_{\pi(1)}} \otimes \mathbf{e}_{i_{\pi(2)}} \otimes \cdots \otimes \mathbf{e}_{i_{\pi(2j)}} \quad (15)$$

by summing over the $(2j)!$ elements of the permutation group \mathfrak{S}_{2j} . The N_{jm} distinct terms are mutually orthonormal with regard to the standard inner product on the unsymmetrized $[V_{1/2}]^{\otimes 2j}$, so computing the inner product from this conventional tensor-product side makes

$$\langle \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m} | \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m} \rangle = (N_{jm})^{-2} N_{jm} = (N_{jm})^{-1}. \quad (16)$$

To confirm the identification, observe that $J_- \mathbf{e}_1 = \mathbf{e}_2$, $J_- \mathbf{e}_2 = 0$, and so

$$\begin{aligned}
J_- |j, m\rangle &= \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} J_- (\mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m}) \\
&= \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} (j+m) \mathbf{e}_1^{j+m-1} \mathbf{e}_2^{j-m+1} \\
&= \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} (j+m) \sqrt{\frac{(j+m-1)!(j-m+1)!}{(2j)!}} |j, m-1\rangle \\
&= \sqrt{(j+m)(j-m+1)} |j, m-1\rangle
\end{aligned} \tag{17}$$

as it should.

Now let $\psi_i = \alpha_i \mathbf{e}_1 + \beta_i \mathbf{e}_2$. Set $z_i = -\beta_i/\alpha_i$, and expand out a decomposable state as

$$\Psi \equiv \psi_{i_1} \odot \cdots \odot \psi_{i_{2j}} = \left(\prod_{i=1}^{2j} \alpha_i \right) a_{j-m} \mathbf{e}_1^{j+m} \mathbf{e}_2^{j-m}, \tag{18}$$

where a_{j-m} is the $(j-m)$ -th elementary symmetric function of the $-z_i$. In other words

$$\sum_{n=0}^{2j} z^{2j-n} a_n = \prod_{i=1}^{2j} (z - z_i). \tag{19}$$

We therefore have

$$\langle j, m | \Psi \rangle = \left(\prod_{i=1}^{2j} \alpha_i \right) a_{j-m} \sqrt{\frac{(j+m)!(j-m)!}{(2j)!}}. \tag{20}$$

or

$$a_{j-m} = \langle j, m | \Psi \rangle \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} \left(\prod_{i=1}^{2j} \alpha_i \right)^{-1}. \tag{21}$$

The common factor $\prod_{i=1}^{2j} \alpha_i = \langle j, j | \Psi \rangle$ does not affect the location of the zeros, so we can replace the a_{j-m} by Majorana's c_{j-m} (which are $\langle j, j | \Psi \rangle a_{j-m}$). Thus given the components $\langle j, m | \Psi \rangle$ we can solve for the roots of $P_\Psi(z) = \sum_{n=0}^{2j} z^{2j-n} c_n = 0$ and construct the α_i, β_i up to an overall phase as before.

The Majorana polynomial $P_\Psi(z)$ for a given $|\Psi\rangle$ has a physical interpretation as the holomorphic spin-coherent-state wavefunction representation of $|\Psi\rangle$. This wavefunction is obtained by first defining a family of spin coherent states

$$|z\rangle = \exp(\bar{z} J_+) |j, -j\rangle, \quad \langle z| = \langle j, -j| \exp(z J_-) \equiv |z\rangle^\dagger. \tag{22}$$

These states are not normalized, but have the advantage that the $\langle z|$ are holomorphic in the parameter z — *i.e.*, they depend on z but not on \bar{z} . The coherent-state wavefunction

$\psi(z) \stackrel{\text{def}}{=} \langle z|\psi\rangle$ corresponding to a state $|\psi\rangle$ is then a holomorphic function. The label z can be identified as the complex stereographic co-ordinate of the spin direction on the two-sphere, with $z = 0$ corresponding to the south pole (spin down) and $z = \infty$ to the north pole (spin up). (Strictly speaking $|\infty\rangle$ is undefined, and one needs two families of coherent states with a transition function to capture every spin direction — see for example [11]. This technicality is not relevant for what follows however.)

The inner product of two states $|\psi\rangle$ and $|\chi\rangle$ may be evaluated in terms of their wavefunctions as

$$\langle\psi|\chi\rangle = \frac{2j+1}{2\pi i} \int_{\mathbb{C}} \frac{d\bar{z} \wedge dz}{(1+|z|^2)^{2j+2}} \overline{\psi(z)} \chi(z). \quad (23)$$

Normalizable wavefunctions are therefore polynomials in z of degree less than or equal to $2j$. In particular

$$\langle z|j, m\rangle = \sqrt{\frac{(2j)!}{(j-m)!(j+m)!}} z^{j+m}, \quad (24)$$

and the wavefunction of coherent state $|\zeta\rangle$ is the polynomial

$$\langle z|\zeta\rangle = (1 + z\bar{\zeta})^{2j}. \quad (25)$$

When acting on the holomorphic wavefunctions then $\mathfrak{su}(2)$ generators J_3 and $J_{\pm} = J_1 \pm iJ_2$ become

$$\begin{aligned} J_+ &\rightarrow -z^2 \frac{\partial}{\partial z} + 2jz \\ J_- &\rightarrow \frac{\partial}{\partial z}, \\ J_3 &\rightarrow z \frac{\partial}{\partial z} - j. \end{aligned} \quad (26)$$

It is straightforward to verify that with respect to the inner product (23) we have $J_3^\dagger = J_3$ and $J_\pm^\dagger = J_\mp$.

Now from (6) and (24) we have

$$\begin{aligned} \Psi(z) \equiv \langle z|\Psi\rangle &= \sum_m \langle z|j, m\rangle \langle j, m|\Psi\rangle \\ &= \sum_{m=-j}^j c_{j-m} z^{j+m} \\ &= P_\Psi(z). \end{aligned}$$

The Majorana polynomial is therefore precisely the coherent state wavefunction. For each zero z_i of the coherent state wavefunction, its *antipode* $-1/\bar{z}_i$ is the stereographic coordinate

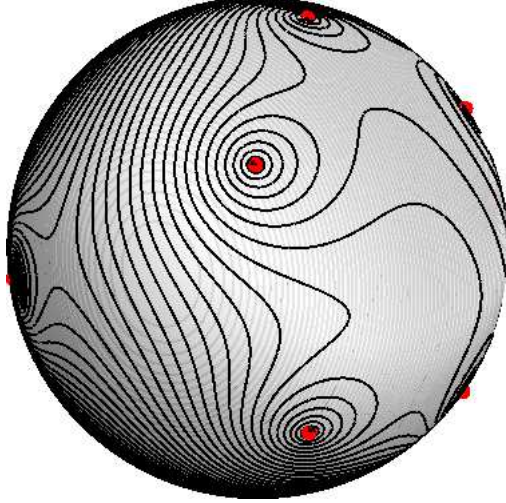


FIG. 1: A contour plot of $\sqrt{|\psi(z, \bar{z})|}$ on the two-sphere for a typical spin state $|\psi\rangle$. The location of its zeros is highlighted in red. The Majorana points of $|\psi\rangle$ are the antipodes of these zeros.

of the direction of one of the component spin-1/2's. These antipodes are known as Majorana points [16, 17].

In the following we sometimes find it convenient to use *normalized* coherent states

$$|z\rangle_N = \frac{1}{(1 + |z|^2)^j} \exp(\bar{z}J_+) |j, -j\rangle, \quad {}_N\langle z| = \frac{1}{(1 + |z|^2)^j} \langle j, -j| \exp(zJ_-) = |z\rangle_N^\dagger \quad (27)$$

and the corresponding non-holomorphic coherent-state wavefunctions

$$\psi(z, \bar{z}) = {}_N\langle z|\psi\rangle.$$

In terms of these non-holomorphic wavefunctions the inner product becomes

$$\langle\psi|\chi\rangle = \frac{2j+1}{2\pi i} \int_{\mathbb{C}} \frac{d\bar{z} \wedge dz}{(1 + |z|^2)^2} \overline{\psi(z, \bar{z})} \chi(z, \bar{z}). \quad (28)$$

The integral now involves only the usual area form on the two-sphere expressed in stereographic coordinates. The normalized wavefunction $\psi(z, \bar{z})$ is therefore the probability amplitude for finding the spin- j pointing in the direction z .

We can describe a spin- j state up to an overall phase by either specifying the zeros z_i of its spin coherent state wavefunction, or by specifying the Majorana points, *i.e.* the directions on the Riemann sphere of its component spin-1/2 factors. Because the spin directions are the antipodes $w_i = -1/\bar{z}_i$ of the zeros, the normalized spin-1/2 state that points in the direction w has wavefunction

$$\psi_w(z, \bar{z}) = \frac{1}{\sqrt{1 + |z|^2}} \frac{1}{\sqrt{1 + |w|^2}} (1 + z\bar{w}). \quad (29)$$

This is just the wavefunction for the state $|w\rangle_N$. Similarly we define

$$\begin{aligned} |\{w_i\}\rangle_N &\equiv |w_1, w_2, \dots, w_{2j}\rangle_N \\ &= \frac{1}{\mathcal{N}} |w_1\rangle \odot |w_2\rangle \odot \dots \odot |w_{2j}\rangle \end{aligned} \quad (30)$$

to be a normalized spin- j state with its $2j$ spin-1/2 components pointing in the directions w_i . Here, \mathcal{N} is a w_i dependent normalization factor given by

$$\mathcal{N}^2 = \langle \{w_i\} | \{w_i\} \rangle = \frac{1}{(2j)!} \sum_{\pi \in \mathfrak{S}} \prod_{i=1}^{2j} (1 + w_i \bar{w}_{\pi(i)}). \quad (31)$$

The corresponding wavefunction is

$${}_N \langle z | w_1, w_2, \dots, w_{2j} \rangle_N = (1 + |z|^2)^{-j} \mathcal{N}^{-1} \prod_{i=1}^{2j} (1 + z \bar{w}_i). \quad (32)$$

III. BERRY TRANSPORT IN THE MAJORANA REPRESENTATION

Non-abelian Berry transport is a generalization of the usual Berry adiabatic transport to the case of degenerate energy eigenvalues [3]. Consider the adiabatic evolution of a state

$$|\psi(t)\rangle = a_n(t) |n, t\rangle \quad (33)$$

that lies in a subspace $V(t)$ spanned by a orthonormal frame $|n, t\rangle, n = 1, \dots, N$, of degenerate eigenstates of a Hamiltonian $H(t)$. If $H(t)$ varies slowly, the resulting adiabatic evolution leads to the coefficients being given by

$$a_n(t) = U_{nm}(t) a_m(0) \exp \left\{ -i \int_0^t E(t) dt \right\}, \quad (34)$$

where $E(t)$ is the common eigenvalue, and

$$U_{nm}(t) = \left[\mathcal{P} \exp \left\{ - \int_0^t \mathcal{A} \right\} \right]_{nm} \quad (35)$$

is a unitary matrix that generalizes the usual Berry phase. The symbol \mathcal{P} indicates a path-ordered integral and the non-abelian Berry connection

$$\mathcal{A}_{nm} = \langle n, t | d | m, t \rangle = -\bar{\mathcal{A}}_{nm} \quad (36)$$

is a skew-hermitian matrix-valued one-form. In the special case that degenerate subspace is one-dimensional it reduces to the abelian Berry connection.

We wish to find expressions for \mathcal{A}_{nm} in the Majorana parametrisation. The one dimensional (Abelian) case was obtained by Hannay [12]. He starts from

$$d|\{w_i\}\rangle = \frac{1}{(2j)!} \sum_{\pi \in \mathfrak{S}_{2j}} \sum_i |w_{\pi(1)}\rangle \otimes \cdots (d|w_{\pi(i)}\rangle) \cdots \otimes |w_{\pi(2j)}\rangle \quad (37)$$

where, from $|w_i\rangle = \bar{w}_i|\uparrow\rangle + |\downarrow\rangle$ we have $d|w_i\rangle = d\bar{w}_i|\uparrow\rangle$, and

$$\mathcal{A} = i \operatorname{Im} \left(\frac{\langle \{w_i\} | d|\{w_i\}\rangle}{\langle \{w_i\} | \{w_i\}\rangle} \right). \quad (38)$$

He obtains

$$\mathcal{A} = i \operatorname{Im} \frac{\sum_{\pi} [\prod_k (1 + w_k \bar{w}_{\pi(k)}) \sum_k (w_k d\bar{w}_{\pi(k)}) / (1 + w_k \bar{w}_{\pi(k)})]}{\sum_{\pi} [\prod_k (1 + w_k \bar{w}_{\pi(k)})]}. \quad (39)$$

For $j = 1/2$, for example, we have

$$\mathcal{A} = i \operatorname{Im} \left(\frac{\langle w | d|w\rangle}{\langle w | w\rangle} \right) = \frac{1}{2} \frac{w d\bar{w} - \bar{w} dw}{1 + \bar{w} w}, \quad d\mathcal{A} = \frac{dw \wedge d\bar{w}}{(1 + \bar{w} w)^2}. \quad (40)$$

The expression for $d\mathcal{A}$ is i times one-half the area form on the two-sphere, and so we find that familiar result that in a cyclic evolution the accumulated phase is one-half of the area swept out by the spin.

For a general value of j consider the evolution of the $E = m$ eigenstate of $H = \mathbf{J} \cdot \hat{\mathbf{n}}$ as the unit vector $\hat{\mathbf{n}}$ varies. In the Majorana parametrisation, $j + m$ of the w_i 's lie at the point w corresponding to the unit vector $\hat{\mathbf{n}}$ and $j - m$ of the w_i lie at the antipodal point $w' = -1/\bar{w}$. Thus equation (39) becomes,

$$\mathcal{A} = \frac{1}{2}(j + m) \frac{w d\bar{w} - \bar{w} dw}{1 + \bar{w} w} + \frac{1}{2}(j - m) \frac{w' d\bar{w}' - \bar{w}' dw'}{1 + \bar{w}' w'}. \quad (41)$$

For a cyclic evolution the accumulated phase is $[(j + m) - (j - m)]/2 = m$ times the area swept out by the point w — again a familiar result [13].

Now consider the non-abelian extension of Hannay's formula in which Berry connection becomes a one-form \mathcal{A} that takes its values in the Lie algebra $\mathfrak{u}(n)$. We can evaluate its skew-hermitian matrix elements in the Majorana parametrisation by extending (39). After some work we find that the off diagonal elements of the connection are

$$\begin{aligned} \mathcal{A}_{rs} &= \frac{\langle \{w_i^r\} | d|\{w_i^s\}\rangle}{\sqrt{\langle \{w_i^r\} | \{w_i^r\}\rangle} \sqrt{\langle \{w_i^s\} | \{w_i^s\}\rangle}} \quad (r \neq s) \\ &= \frac{\sum_{\pi} \prod_k (1 + w_k^r \bar{w}_{\pi(k)}^s) \sum_k (w_k^r d\bar{w}_{\pi(k)}^s) / (1 + w_k^r \bar{w}_{\pi(k)}^s)}{\sqrt{\sum_{\pi} [\prod_k (1 + w_k^r \bar{w}_{\pi(k)}^r)]} \sqrt{\sum_{\pi} [\prod_k (1 + w_k^s \bar{w}_{\pi(k)}^s)]}}. \end{aligned} \quad (42)$$

and the diagonal elements are

$$\begin{aligned}\mathcal{A}_{rr} &= i \frac{\text{Im}\langle\{w_i^r\}|\text{d}|\{w_i^r\}\rangle}{\langle\{w_i^r\}|\{w_i^r\}\rangle} \\ &= \frac{\sum_{\pi} \text{Im} \left[\prod_k (1 + w_k^r \bar{w}_{\pi(k)}^r) \sum_k (w_k^r \text{d}\bar{w}_{\pi(k)}^r) / (1 + w_k^r \bar{w}_{\pi(k)}^r) \right]}{\sum_{\pi} \left[\prod_k (1 + w_k^r \bar{w}_{\pi(k)}^r) \right]}.\end{aligned}\quad (43)$$

The expressions in equations (42) and (43) are, in general, rather complicated. Our interest, however, is in the evolution of Kramers-degenerate pairs. We therefore restrict ourselves to the time-reversal invariant hamiltonians, and to half-integer j for which the Kramers pair of states $|\Psi\rangle$ and $\mathcal{T}|\Psi\rangle$ are degenerate and mutually orthogonal.

The time reversal operator on a general spin state is

$$\mathcal{T} = \exp\{-i\pi J_2\}\mathcal{K} \quad (44)$$

where \mathcal{K} denotes complex conjugation. On a spin-1/2 coherent state it acts as

$$\mathcal{T}|w\rangle = w| - 1/\bar{w}\rangle \quad (45)$$

and this action extends to the general Majorana-parametrisation tensor product state.

Using the states $|\Psi\rangle$, $\mathcal{T}|\Psi\rangle$ as basis, the Berry connection becomes a two-by-two traceless skew-hermitian matrix,

$$\mathcal{A} = \begin{pmatrix} \mathcal{A}_0 & -\mathcal{A}_1 \\ \bar{\mathcal{A}}_1 & -\mathcal{A}_0 \end{pmatrix}. \quad (46)$$

The tracelessness of \mathcal{A} is a consequence of time-reversal; it implies that the diagonal Abelian phases for a Kramers pair are complex-conjugates of each other.

In the Majorana parametrisation

$$\bar{\mathcal{A}}_1 = \frac{\langle\{w_i\}|\text{d}|\mathcal{T}\{w_i\}\rangle}{\sqrt{\langle\{w_i\}|\{w_i\}\rangle}\sqrt{\langle\mathcal{T}\{w_i\}|\mathcal{T}\{w_i\}\rangle}} = \frac{\sum_{\pi} [\prod_k (w_{\pi(k)} - w_k) \sum_k (\text{d}w_k) / (w_{\pi(k)} - w_k)]}{\sum_{\pi} [\prod_k (1 + \bar{w}_k w_{\pi(k)})]} \quad (47)$$

For eigenstates of $H = \mathbf{J} \cdot \hat{\mathbf{n}}$ (47) simplifies considerably. Again, there are $j + m$ Majorana points w and $j - m$ points at $w' = -1/\bar{w}$. The numerator contains the factor $[\prod_{k,k \neq j} (w_{\pi(k)} - w_k)]$, which can only be non-zero for permutations that swap the w and w' except at most a single point that may map to itself (recall that $2j$ is odd). As a consequence the off-diagonal term is non-zero only for $m = 1/2$ states. When $m \neq 1/2$ the Berry

transport is purely Abelian, in the sense that there exists a fixed basis whose states are only multiplied by a phase for any loop in Hamiltonian space.

Consider, for example rotations of $\hat{\mathbf{n}}$ about the z axis. We have $w_i \rightarrow w_i \exp i\phi$ and $dw_i = iw_i d\phi$ and equation 47) becomes

$$\mathcal{A}_1 = \frac{\sum_P [\prod_k (w_{\pi(k)} - w_k) \sum_k w_k / (w_{\pi(k)} - w_k)]}{\sum_P [\prod_k (1 + \bar{w}_k w_{\pi(k)})]} id\phi. \quad (48)$$

For a $m = 1/2$ state with Majorana points at $w = \tan(\theta/2) \exp\{i\phi\}$ and $w' = \cot(\theta/2) \exp\{-i\phi\}$ we get

$$\begin{aligned} \mathcal{A}_1 &= \frac{(n+1)!(n+1)!}{n!(n+1)!} \frac{(1 + ww')^{2n} / w'^{2n}}{(1 + ww')^{2n+1} / (ww')^n} w(id\phi) \\ &= (n+1) \frac{w^n}{w'^n} \frac{1}{1 + ww'} w(id\phi) \\ &= \exp[i(2n+1)\phi] \frac{(n+1)}{2} \sin(\theta)(id\phi) \end{aligned} \quad (49)$$

where $2n+1 = 2j$ is the total number of Majorana points. We may redefine the basis states so as to absorb the phase factor so that

$$\mathcal{A}_1 = \frac{(n+1)}{2} \sin(\theta)(id\phi) = \frac{1}{2} \left(j + \frac{1}{2} \right) \sin(\theta)(id\phi), \quad (50)$$

and this expression agrees with a result in [5].

IV. KATO'S EQUATION

The Berry-connection one-form allows us to adiabatically evolve states, but, because it involves continually making a choice of basis, it is not always the most convenient method for numerical computation. An alternative tool is provided by the operator $P(t)$ that projects us into our space $V(t)$ of eigenstates of $H(t)$ with a common eigenvalue $E(t)$. This subspace evolves with the parameters in $H(t)$, and the Berry-transport condition [3] is

$$P(t) \frac{\partial}{\partial t} |\psi(t)\rangle = 0. \quad (51)$$

Intuitively, the Berry condition says that we keep projecting the state down into the evolving degenerate subspace. This process is completely equivalent to transport *via* \mathcal{A}_{nm} .

Using the projection operators we can approximate the adiabatic evolution as

$$|\psi(t)\rangle = P(t)P(t-\epsilon)P(t-2\epsilon)\cdots P(0)|\psi(0)\rangle. \quad (52)$$

For finite ϵ , this sequence of successive projections is not norm-preserving, but in the limit $\epsilon \rightarrow 0$ it becomes so.

We now observe that

$$\begin{aligned} \frac{1}{\epsilon} \{ |\psi(t+\epsilon)\rangle - |\psi(t)\rangle \} &= \frac{1}{\epsilon} \{ P(t+\epsilon) - 1 \} P(t) P(t-\epsilon) \cdots P(0) |\psi(0)\rangle \\ &= \frac{1}{\epsilon} \{ P(t+\epsilon) - P(t) \} P(t) P(t-\epsilon) \cdots P(0) |\psi(0)\rangle. \end{aligned} \quad (53)$$

Here we have used the projection-operator property $P(t)^2 = P(t)$. On taking the limit $\epsilon \rightarrow 0$, we are lead to evolution equation

$$\frac{\partial}{\partial t} |\psi(t)\rangle = \dot{P}(t) |\psi(t)\rangle. \quad (54)$$

Let us confirm that this evolution satisfies equation (51): from $P^2 = P$ we have $\dot{P}P + P\dot{P} = \dot{P}$, and so

$$\begin{aligned} P \frac{\partial}{\partial t} |\psi\rangle_t &= P \dot{P}(t) |\psi(t)\rangle \\ &= (\dot{P}P - \dot{P}) |\psi\rangle \\ &= (\dot{P} - \dot{P}) |\psi\rangle \\ &= 0. \end{aligned} \quad (55)$$

In passing from the second line to the third we have used $P|\psi\rangle = |\psi\rangle$ for $|\psi\rangle$ in the degenerate subspace $V(t)$.

Although equation (54) is very simple, it has a formal drawback in that it does not provide a manifestly unitary state evolution. The operator $P(t)$ is hermitian, and so therefore is $\dot{P}(t)$. For unitary evolution we would expect the operator on the right hand side of (54) to be *skew* hermitian. We can, however, equivalently write (54) as

$$\frac{\partial}{\partial t} |\psi\rangle_t = [\dot{P}(t), P(t)] |\psi(t)\rangle. \quad (56)$$

We have already seen that the the added term $P\dot{P}$ vanishes when acting on states in the degenerate eigenspace. Now the commutator of two hermitian operators on the right-hand side *is* skew hermitian, so this version of the evolution equation does provide a manifestly unitary evolution. Equation (56) governing the non-abelian Berry transport is known as *Kato's equation* [15] after Tosio Kato who obtained it in 1950.

Now our interest is in the evolution of the spin in a molecule that is rotating in space. For a fixed orientation of the molecule, the spin Hamiltonian is a polynomial

$$H(\mathbf{J}) = \sum_{m=0}^{2j} \sum_{i_1, \dots, i_m=1}^3 a_{i_1 i_2 \dots i_m} J_{i_1} J_{i_2} \cdots J_{i_m} \quad (57)$$

in the space-fixed components J_i of the spin angular momentum operator. The effect of a real space rotation R on the molecule is to change $J_i \rightarrow R_{ij}^{-1} J_j$ in this polynomial while keeping the coefficients $a_{i_1 i_2 \dots i_m}$ fixed. Now for each R there is a unitary operator $U[R]$ that implements the rotation in the $2j + 1$ dimensional Hilbert space:

$$R_{ij}^{-1} J_j = U[R] J_i U^{-1}[R], \quad (58)$$

so as the molecule rotates we can write

$$H(t) = U[R(t)] H(0) U[R(t)]^{-1}, \quad (59)$$

where $U(t) = U[R(t)]$. (This $U(t)$ is not to be confused with the adiabatic evolution operator $U_{nm}(t)$ in equation (35).) The same operator evolves the projection

$$P(t) = U(t) P(0) U(t)^{-1}, \quad (60)$$

and we can work in a frame rotating with the molecule by setting $|\psi(t)\rangle = U(t)|\phi(t)\rangle$. In this frame Kato's equation becomes

$$\frac{\partial}{\partial t} |\phi(t)\rangle = -P(0) U^{-1} \dot{U} P(0) |\phi(t)\rangle. \quad (61)$$

The evolution given by (61) now all takes place within $V(0)$ and $|\phi_t\rangle = G(t)|\phi_0\rangle$, where the propagator $G(t)$ is be the time-ordered exponential

$$\begin{aligned} G(t) &= \mathcal{P} \exp \left(- \int_0^t P(0) K(s) P(0) ds \right) \\ &= \lim_{\epsilon \rightarrow 0} \{ P(0) (1 - \epsilon K(t)) P(0) (1 - \epsilon K(t - \epsilon)) P(0) \cdots P(0) (1 - \epsilon K(0)) P(0) \}, \end{aligned} \quad (62)$$

where $K = U^{-1} \dot{U}$. From (62) we can see that $G(t) P(0) G(t)^{-1} = P(0)$.

V. ACTION PRINCIPLE AND EQUATIONS OF MOTION

The projection $P(0)$ in (62) acts as the identity operator on the subspace $V(0)$, and is effectively the quantum evolution of a state restricted to $V(0)$. We can therefore represent (62) by means of a Feynman path integral over trajectories in some suitable classical system.

As in the previous section we assume time-reversal invariance and half-integer spin, so that by Kramers' theorem each energy level is doubly-degenerate and spanned by $|\phi(0)\rangle$ and $\mathcal{T}|\phi(0)\rangle$ (which we denote here as $|\mathcal{T}\phi(0)\rangle$). In such a space the initial projection operator $P(0)$ is

$$P(0) = |\phi(0)\rangle\langle\phi(0)| + |\mathcal{T}\phi(0)\rangle\langle\mathcal{T}\phi(0)|. \quad (63)$$

Since $V(0)$ is two-dimensional, the natural path integral is the spin-coherent-state path integral for $SU(2)$.

To obtain the path integral we let $\lambda \in \mathbb{C}P^1$ be the stereographic complex coordinate of a point on the Riemann sphere and set

$$|\lambda\rangle_N = (1 + \lambda\bar{\lambda})^{-1/2}(|\mathcal{T}\phi(0)\rangle + \bar{\lambda}|\phi(0)\rangle) \quad (64)$$

$$\langle\lambda|_N = (1 + \lambda\bar{\lambda})^{-1/2}(\langle\mathcal{T}\phi(0)| + \lambda\langle\phi(0)|). \quad (65)$$

These are analogous to the spin-1/2 coherent states in which $|\mathcal{T}\phi(0)\rangle$ and $|\phi(0)\rangle$ are playing the roles of the spin down and spin up states respectively.

We now write the projection operator $P(0)$ as the (overcomplete) resolution

$$P(0) = \frac{2}{4\pi} \int_{\mathbb{C}P^1} \frac{2 d\bar{\lambda} \wedge d\lambda}{i(1 + \lambda\bar{\lambda})^2} |\lambda\rangle\langle\lambda|_N, \quad (66)$$

and with it construct, by time-slicing with $P(0)$, what is essentially a spin-1/2 “coherent” state path-integral [11] containing the action

$$S[\lambda, \bar{\lambda}] = \int_0^T dt \left(\frac{1}{2} \frac{\bar{\lambda}\dot{\lambda} - \dot{\bar{\lambda}}\lambda}{1 + \lambda\bar{\lambda}} - \mathcal{A}_0(\lambda, \bar{\lambda}) \right), \quad (67)$$

with $\mathcal{A}_0 \equiv \langle\lambda|K|\lambda\rangle$.

We might attempt to evaluate this path integral by some technique. However, when the Hamiltonian term is *linear* in the Lie algebra generators, as it is in this case, then we know that the *classical* equations of motion give the exact quantum evolution (See for example [18, 19]).

These equations are

$$\frac{d\lambda}{dt} = (1 + \lambda\bar{\lambda})^2 \frac{\partial \mathcal{A}_0}{\partial \bar{\lambda}} \quad (68)$$

$$\frac{d\bar{\lambda}}{dt} = -(1 + \lambda\bar{\lambda})^2 \frac{\partial \mathcal{A}_0}{\partial \lambda} \quad (69)$$

Now, from the construction of $|\lambda\rangle$, we can write

$$(1 + \lambda\bar{\lambda})\frac{\partial}{\partial\bar{\lambda}}\langle\lambda|X|\lambda\rangle = -\langle\lambda|X\mathcal{T}|\lambda\rangle \quad (70)$$

for any operator X . In particular we can rewrite (69) as

$$\frac{d\lambda}{dt} = -(1 + \lambda\bar{\lambda})\mathcal{A}_1 \quad (71)$$

$$\frac{d\bar{\lambda}}{dt} = -(1 + \lambda\bar{\lambda})\bar{\mathcal{A}}_1 \quad (72)$$

where $\mathcal{A}_1(\lambda, \bar{\lambda}) \equiv \langle\lambda|K\mathcal{T}|\lambda\rangle$. We now know the time evolution of $\lambda(t)$, and hence the time evolution of $|\phi(t)\rangle$.

To see how changes in λ and $\bar{\lambda}$ translate into changes in the location of the zeros z_i , or equivalently the Majorana points $w_i = -1/\bar{z}_i$ we observe that

$$|\lambda\rangle_N = e^{i\gamma}|\{w_i\}\rangle_N \quad (73)$$

for some phase γ , and so

$$\begin{aligned} \psi(z, \bar{\lambda}) &= e^{i\gamma}\mathcal{N}^{-1}(1 + |z|^2)^{-j} \prod_{i=1}^{2j}(1 + z\bar{w}_i) \\ &= Q \prod_{i=1}^{2j}(1 + z\bar{w}_i), \end{aligned} \quad (74)$$

where $Q = e^{i\gamma}\mathcal{N}^{-1}(1 + |z|^2)^{-j}$. The last form reminds us that the roots of the wavefunction $\psi(z, \bar{\lambda})$ are at $z_i = -1/\bar{w}_i$. Assume for now that the zeros are all non-degenerate — that is, $z_i \neq z_j$ if $i \neq j$. Consider a root $z_k(\bar{\lambda})$ of $\langle z|\lambda\rangle$, and recall that the zeros of $\langle z|\lambda\rangle$ depend only on $\bar{\lambda}$ while those of $\langle\lambda|z\rangle$ depend only on λ . Let $\bar{\lambda} \rightarrow \bar{\lambda} + \delta\bar{\lambda}$ and expand $z_k(\bar{\lambda} + \delta\bar{\lambda})$ to first order as

$$z_k(\bar{\lambda} + \delta\bar{\lambda}) = z_k(\bar{\lambda}) + \frac{dz_k}{d\bar{\lambda}}\delta\bar{\lambda}, \quad (75)$$

For $z_k(\lambda + \delta\bar{\lambda})$ to remain a root, we must have

$$\psi\left(z_k + \frac{dz_k}{d\bar{\lambda}}\delta\bar{\lambda}, \bar{\lambda} + \delta\bar{\lambda}\right) = 0. \quad (76)$$

Expanding (76) to first order and using $\psi(z_k, \bar{\lambda}) = 0$, we find [6, 20]

$$\frac{dz_k}{d\bar{\lambda}} = -\frac{\partial\psi}{\partial\bar{\lambda}}\left(\frac{\partial\psi}{\partial z}\right)^{-1}\bigg|_{z_k}. \quad (77)$$

The denominator of (77) is obtained by straightforward differentiation of (74) to be

$$\left. \frac{\partial \psi}{\partial z} \right|_{z_k} = -Q \bar{w}_k^{2-2j} \prod_{i \neq k} (\bar{w}_k - \bar{w}_i), \quad (78)$$

and the numerator is

$$\left. \frac{d\psi}{d\lambda} \right|_{z_k} = -(1 + |\lambda|^2)^{-1} e^{-2i\gamma} Q \bar{w}_k^{-2j} \prod_i (1 + w_i \bar{w}_k). \quad (79)$$

Combining equations (76), (78), (79), and using that

$$\frac{dz_k}{d\bar{\lambda}} = \frac{d}{d\bar{\lambda}} \left(-\frac{1}{\bar{w}_k} \right) = -\frac{1}{\bar{w}_k^2} \frac{d\bar{w}_k}{d\bar{\lambda}}, \quad (80)$$

we arrive at differential equations for the Majorana points w_k in terms of λ ,

$$(1 + \lambda \bar{\lambda}) \frac{dw_k}{d\lambda} = e^{2i\gamma} (1 + w_k \bar{w}_k) \prod_{i \neq k} \frac{1 + \bar{w}_i w_k}{w_k - w_i}, \quad (81)$$

$$(1 + \lambda \bar{\lambda}) \frac{d\bar{w}_k}{d\bar{\lambda}} = e^{-2i\gamma} (1 + w_k \bar{w}_k) \prod_{i \neq k} \frac{1 + w_i \bar{w}_k}{\bar{w}_k - \bar{w}_i}. \quad (82)$$

Now

$$\frac{dw}{dt} = \frac{dw}{d\lambda} \frac{d\lambda}{dt} = \frac{dw}{d\lambda} (1 + |\lambda|^2) \mathcal{A}_1, \quad (83)$$

where we have used (72), and

$$\mathcal{A}_1 = {}_N \langle \lambda | U^{-1} \dot{U} \mathcal{T} | \lambda \rangle_N = e^{-2i\gamma} {}_N \langle \{w\} | U^{-1} \dot{U} \mathcal{T} | \{w\} \rangle_N. \quad (84)$$

The phase γ cancels leaving us with

$$\begin{aligned} \frac{dw_k}{dt} &= {}_N \langle \{w\} | U^{-1} \dot{U} \mathcal{T} | \{w\} \rangle_N (1 + w_k \bar{w}_k) \prod_{i \neq k} \frac{1 + \bar{w}_i w_k}{w_k - w_i}, \\ \frac{d\bar{w}_k}{dt} &= \overline{{}_N \langle \{w\} | U^{-1} \dot{U} \mathcal{T} | \{w\} \rangle_N} (1 + w_k \bar{w}_k) \prod_{i \neq k} \frac{1 + w_i \bar{w}_k}{\bar{w}_k - \bar{w}_i}. \end{aligned} \quad (85)$$

The equations (85) are quite intricate. To gain some insight, consider some of their properties. We begin by locating possible fixed points of (85). If \dot{w}_k is to be zero there are two possibilities: either the the product $\prod_{i \neq k} (1 + \bar{w}_i w_k) (w_k - w_i)^{-1}$ must vanish, or the factor ${}_N \langle \{w\} | U^{-1} \dot{U} \mathcal{T} | \{w\} \rangle_N$ must vanish. We focus on the first possibility. For this to occur, one of the Majorana points w_i must become antipodal to w_k — that is there is a $w_{k'}(t)$ such that

$$w_{k'}(t) = -\frac{1}{\bar{w}_k(t)}. \quad (86)$$

At that instant, $\dot{w}_k = 0$. But observe that this also hold true under $k \rightarrow k'$, and $\dot{w}_k = 0$ as well. Consequently, both w_k and $w_{k'}$ remain static for all t . As such, antipodal Majorana points are always fixed.

We can understand this by noting that antipodal Majorana points are actually Majorana points that are common to both $|\phi_t\rangle$ and $|\mathcal{T}\phi_t\rangle$. Suppose the Majorana points of $|\phi_t\rangle$ are given by

$$a_1, -1/\bar{a}_1, \dots, a_r, -1/\bar{a}_r, \xi_1, \dots, \xi_p \quad (2r + p = 2j) \quad (87)$$

where the a_i 's come in antipodal pairs. Since \mathcal{T} takes the Majorana points to their antipodes, the a_i 's are preserved; in other words, the Majorana points of $|\mathcal{T}\phi\rangle$ are

$$a_1, -1/\bar{a}_1, \dots, a_r, -1/\bar{a}_r, -1/\bar{\xi}_1, \dots, -1/\bar{\xi}_p. \quad (88)$$

Note that $|\phi_t\rangle$ is a linear combination of $|\phi_0\rangle$ and $|\mathcal{T}\phi_0\rangle$, when $|\phi_t\rangle$ and $|\mathcal{T}\phi_0\rangle$ have any Majorana points in common, then $|\phi_t\rangle$ will also share these Majorana points.

To summarize: if a pair of Majorana points start out being antipodal, then they remain fixed at all times. In future we will factor out these fixed points, and refer to the non-fixed Majorana points as “free” or “dynamical”.

Since the fixed Majorana points do not participate in the dynamics, the requirement in equation (85) of non-degenerate Majorana points can be relaxed to only requiring that none of the free Majorana points ever coincide. This includes states whose fixed antipodal pairs occure more than once (for example, the $|j, 1/2\rangle, |k, -1/2\rangle$ states).

Writing ξ_i for the free Majorana points and $a_i, -1/\bar{a}_i$ for the fixed antipodal pairs as in (87), we find that

$$\begin{aligned} \frac{d\xi_k}{dt} &= {}_N\langle\{a\}, \{\xi\}|U^{-1}\dot{U}\mathcal{T}|\{a\}, \{\xi\}\rangle_N (1 + \xi_k \bar{\xi}_k) \eta \prod_{\substack{1 \leq i \leq p \\ i \neq k}} \frac{1 + \bar{\xi}_i \xi_k}{\xi_k - \xi_i} \\ \frac{d\bar{\xi}_k}{dt} &= \overline{{}_N\langle\{a\}, \{\xi\}|U^{-1}\dot{U}\mathcal{T}|\{a\}, \{\xi\}\rangle_N (1 + \xi_k \bar{\xi}_k)} \bar{\eta} \prod_{\substack{1 \leq i \leq p \\ i \neq k}} \frac{1 + \xi_i \bar{\xi}_k}{\bar{\xi}_k - \bar{\xi}_i} \end{aligned} \quad (89)$$

Here $\eta = \prod_{i=1}^r (-\bar{a}_i/a_i)$ is an a -dependent overall phase, and $|\{a\}, \{\xi\}\rangle$ denotes a state in the Majorana representation with fixed Majorana points $a, -1/\bar{a}$, and free Majorana points ξ . Observe that (89) is well behaved even if ξ_k coincides with one of the a 's, but becomes singular if any ξ_k approaches another free $\xi_{k'}$.

An especially interesting case occurs when only one Majorana point is free and the rest compose antipodal pairs. In this case the equations of motion reduce to

$$\frac{d\xi}{dt} = {}_N\langle\{a\}, \xi|U^{-1}\dot{U}|\mathcal{T}|\{a\}, \xi\rangle_N(1 + \xi\bar{\xi})\eta \quad (90)$$

$$\frac{d\bar{\xi}}{dt} = \overline{{}_N\langle\{a\}, \xi|U^{-1}\dot{U}|\mathcal{T}|\{a\}, \xi\rangle_N}(1 + \xi_k\bar{\xi}_k)\bar{\eta} \quad (91)$$

What is interesting here is that (91) can be derived from an action

$$S[\xi, \bar{\xi}] = \int_0^T ds \left(\frac{1}{2} \frac{\bar{\xi}\dot{\xi} - \xi\dot{\bar{\xi}}}{1 + \xi\bar{\xi}} - {}_N\langle\{a\}, \xi|U^{-1}\dot{U}|\{a\}, \xi\rangle_N \right). \quad (92)$$

The semiclassical equations of motion obtained from this action are

$$\begin{aligned} \frac{d\xi}{dt} &= -(1 + \xi\bar{\xi})^2 \frac{\partial}{\partial \bar{\xi}} {}_N\langle\{a\}, \xi|U^{-1}\dot{U}|\{a\}, \xi\rangle_N \\ \frac{d\bar{\xi}}{dt} &= (1 + \xi\bar{\xi})^2 \frac{\partial}{\partial \xi} {}_N\langle\{a\}, \xi|U^{-1}\dot{U}|\{a\}, \xi\rangle_N, \end{aligned} \quad (93)$$

At first glance equations (91) and (93) look different. That they are, equivalent however, can be verified by using equation (70)

VI. ILLUSTRATION

As an application of our formalism, consider the family of molecular magnets Mn4. The effective Hamiltonian for the $j = 9/2$ molecular spin in the absence of an external field can be written as

$$\mathcal{H} = k_x J_x^2 + k_y J_y^2 + k_z J_z^2, \quad (94)$$

together with small quartic terms that we will ignore. (The small field-coupling between the spins on different molecules will also produce a term linear in J — and therefore time-reversal symmetry breaking — which may be significant. We are, however, also going to ignore this for the moment.) Following [22], we adopt the values $k_x = -k_y = 0.0243\text{K}$, $k_z = -0.59\text{K}$.

First, we look at the configurations of the zeros for the eigenstate wavefunctions of \mathcal{H} , for which there are a total of 5 doubly-degenerate levels when $j = 9/2$. Due to the relatively large quadrupole moment k_z of the z axis, the Hamiltonian is close to that of J_z^2 , and as a result the zeros of the wavefunctions will want to cluster about the poles (see figure 2). But

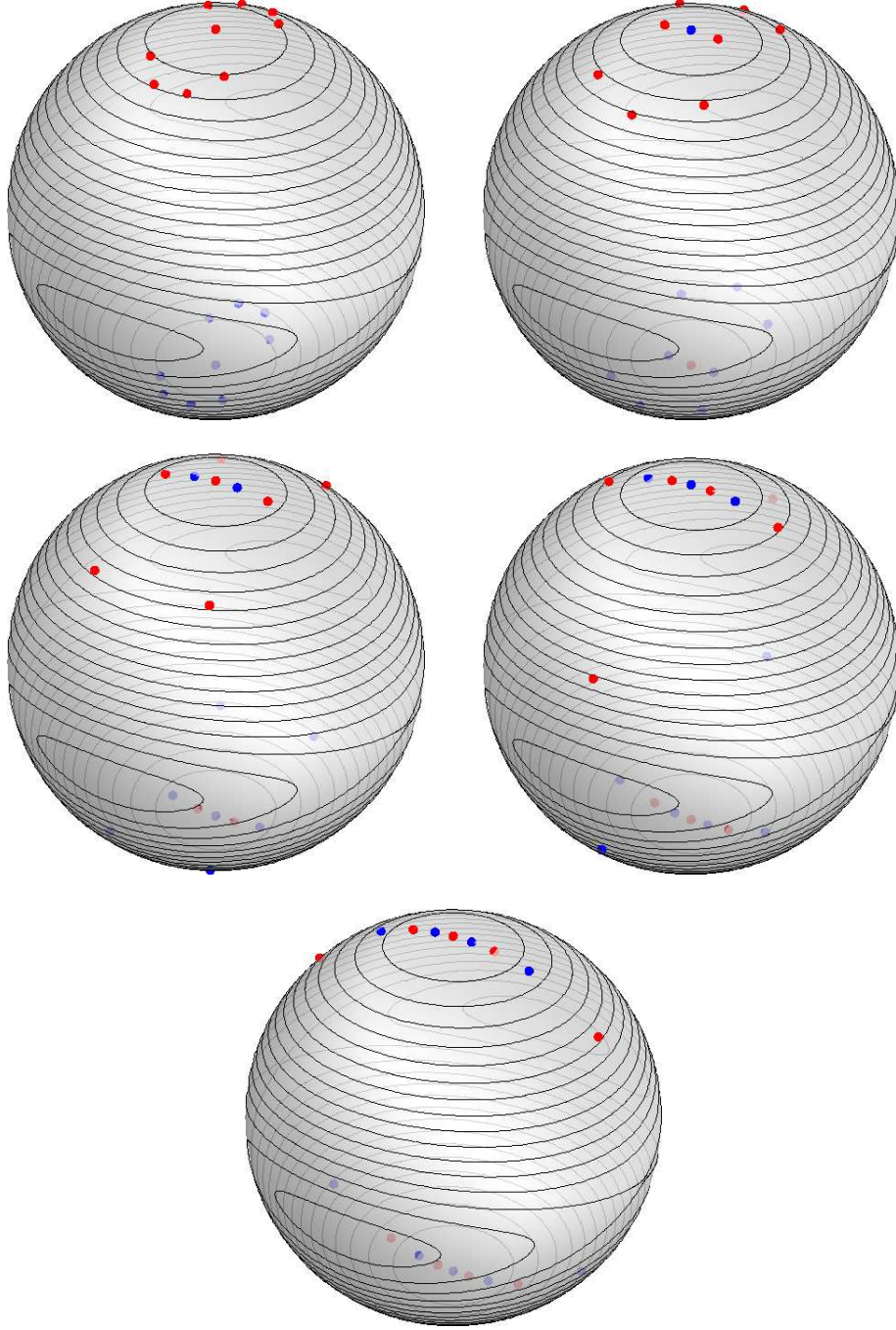


FIG. 2: The zeros of the eigenstate wavefunctions for \mathcal{H} in absence of an applied field, for which the expectation $\langle \mathbf{J} \rangle$ is largest about the z-axis. Blue and red denote the zeros of the eigenstate and its Kramers pair, respectively. In order from left to right and top to bottom, we have (1) ground state, (2) first excited state, (3) second excited state, (4) third excited state, (5) highest state. In the background we have plotted the energy contours of corresponding semiclassical Hamiltonian.

unlike zeros of $\langle z|j, m\rangle$ which simply condense at the poles, the small J_x^2 and J_y^2 terms will cause some repulsion between them. In the background we also display the contours of the “classical” potential landscape defined by the expectation $h(z, \bar{z}) \stackrel{\text{def}}{=} {}_N\langle z|H|z\rangle_N$.

Due to the double degeneracy however, there is a freedom in the choice of the basis of the eigenspace. One particularly illuminating selection is made by putting in a small transverse magnetic field in the $\hat{\mathbf{x}}$ direction and relaxing the field strength to zero. In figure 3 we see that for the ground states the zeros tend to distribute themselves along flow lines $\nabla h(z, \bar{z})$ in a manner such that the two ground states have all their zeros distributed about regions of maximum energy, while for the first excited states a pair of zeros for each state have relocated themselves close to the minima, for the second excited state an additional pair, etc. In addition, for the first, second, and third excited states we find that the zeros about the poles of one state very closely overlap with that of its Kramers pair, and this can have an effect when considering the dynamics their dynamics under adiabatic evolution. We remark however that for this choice of states the magnetization $\langle \mathbf{J} \rangle$ becomes significantly reduced, and may consequently be very difficult to measure.

Now we consider adiabatic holonomy arising from rotations about a fixed axis $\hat{\mathbf{n}} = \sin \eta \cos \gamma \hat{\mathbf{x}} + \sin \eta \sin \gamma \hat{\mathbf{y}} + \cos \eta \hat{\mathbf{z}}$ at an angular velocity of $2\pi/T$. For such rotations we are guaranteed to have the state return to itself (in the corotating frame) after some time τ , which need not coincide in general with the period of rotation T ; the former is gotten by decomposing $PU^{-1}\dot{U}P$ into sigma matrices $x_i\sigma_i$ in the eigenstate basis, for which the period is then found as $2\pi/|x|$. Fixed-axis rotations have been considered before by [5], but their attention is restricted to eigenstates of isotropic Hamiltonians of the form $\hat{\mathbf{n}} \cdot \mathbf{J}$.

The motion of the zeros can be quite complicated. The greatest intricacy occurs for higher levels where the Kramers pairs communicate more strongly. As an illustrative example we plot in figure 4 for one full cycle τ , and for various axis orientations, the trajectories in the corotating frame of the highest-level wavefunction zeros (polarized initially along $\hat{\mathbf{x}}$). Observe that trajectories of nearby axes can exhibit qualitatively different behavior — in particular closed cycles of individual zeros can combine into larger cycles in which the zeros permute locations. These trajectories have been calculated numerically by both using the projection method in Kato’s equation, as well as by solving the equations of motion for the Majorana points, and are found to agree well. (The intricate motion is best appreciated by viewing animations. We have made these available at [21])

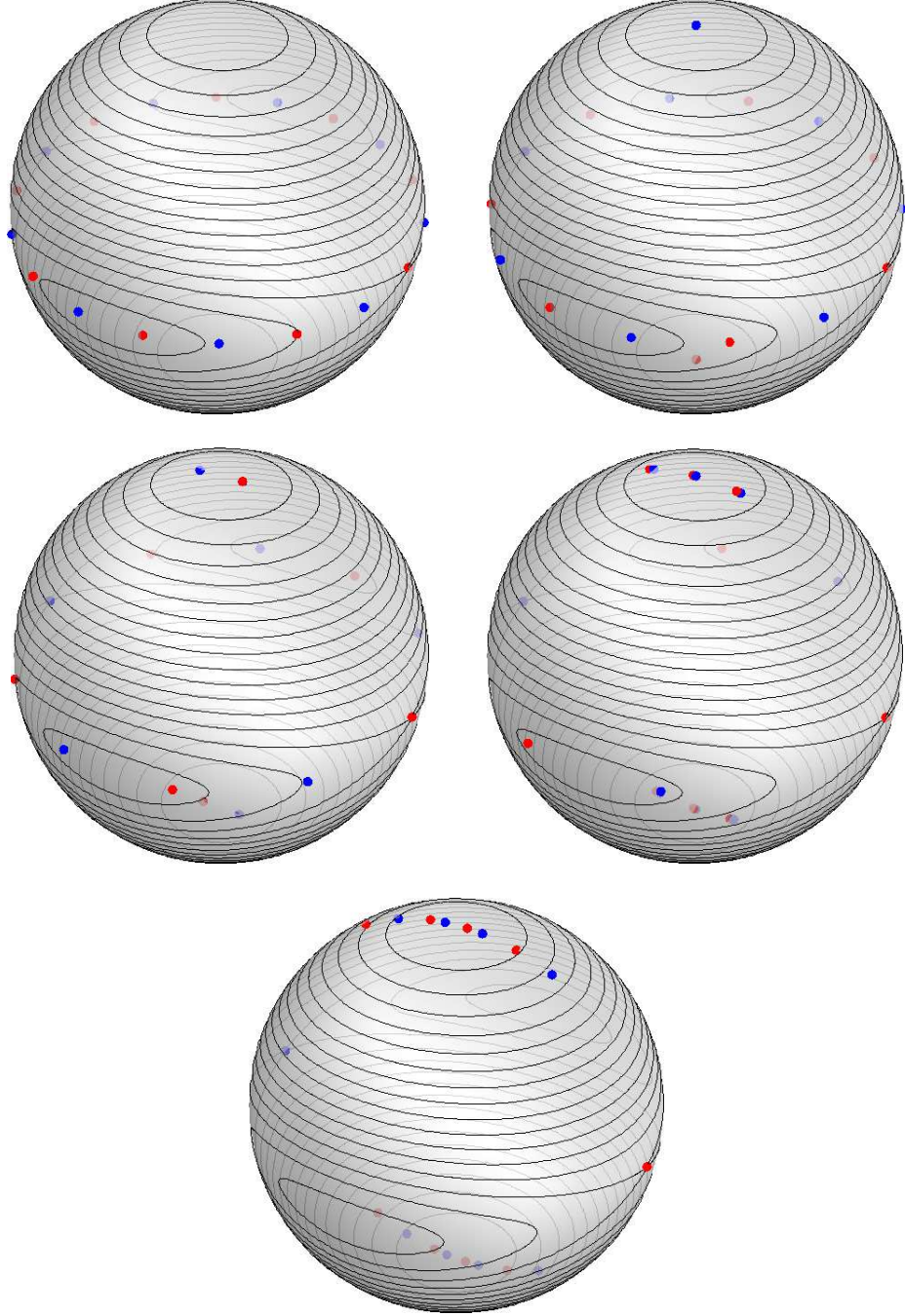


FIG. 3: The zeros of the eigenstate wavefunctions for \mathcal{H} in absence of an applied field, for which the initial states are prepared by polarizing along the $\hat{\mathbf{x}}$. Note that in the first, second, and third excited states the zeros about the poles actually very closely overlap — for example the blue dot in the north pole for the first excited state is actually a pair of blue and red dots.

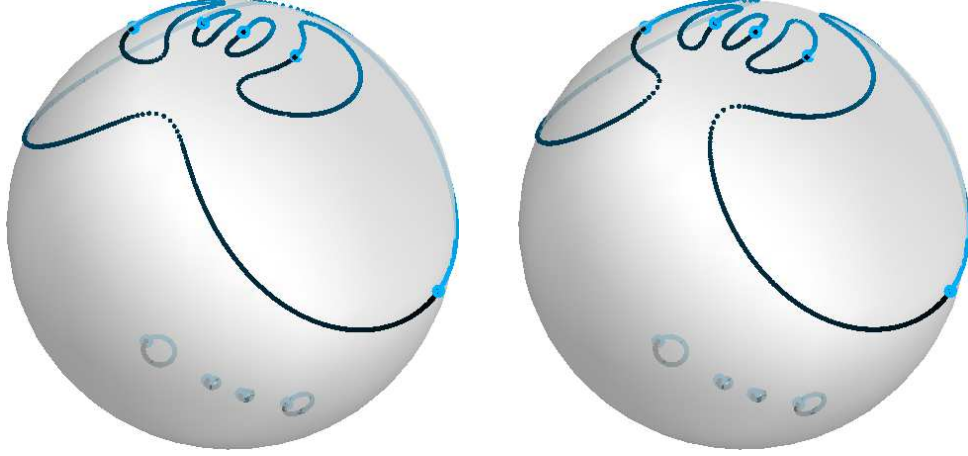


FIG. 4: Trajectories of the zeros, in the corotating frame, for the highest energy level. Lighter blue corresponds to earlier in time, and darker to later. In the left figure the axis was chosen along $\eta = 0.0345\pi$, $\gamma = 0$; and in the right figure the axis was along $\eta = 0.0355\pi$, $\gamma = 0$. A small change in zenith angle has completely changed the topology of the trajectories.

Now consider the time-dependence of the magnetization $\langle \mathbf{J} \rangle$. By spinning the molecule at some frequency $1/T$ about the chosen axis, the magnetic moment may oscillate at a different frequency $1/\tau$, which can be measured by placing pickup coils near the sample. The exact form of the moment oscillation depends on the energy level as well as the choice of initial state within the level.

In figure 5 we look at a sample initially in the ground state, polarized along the $\hat{\mathbf{z}}$ direction. Such a state has a large initial magnetization along $\hat{\mathbf{z}}$ and zero magnetization along the transverse directions. We then rotate the sample about $\hat{\mathbf{x}}$ at a frequency of $2\pi/T$, where T is large compared the timescale of the gap — in this case ≈ 8 K, or $\approx 6 \times 10^{-12}$ seconds. We then calculate $\langle \mathbf{J} \rangle$ in the body frame of the molecule, and we find that while the $\langle J_x \rangle$ and $\langle J_y \rangle$ components do not vary much (being virtually zero), the $\langle J_z \rangle$ component exhibits appreciable oscillations on the timescale of $\tau \approx 165000T$. What one should see in the lab frame then are rapid oscillations of $\langle J_z \rangle$ on the order of T , with an amplitude modulation with period τ .

Finally, in figure 6 we look at a state initially polarized along the $\hat{\mathbf{x}}$ direction and rotated about $\hat{\mathbf{z}}$. The motivation for this is to look at states whose magnetization along the axis of rotation is suppressed. We find that as the energy level becomes higher, the component

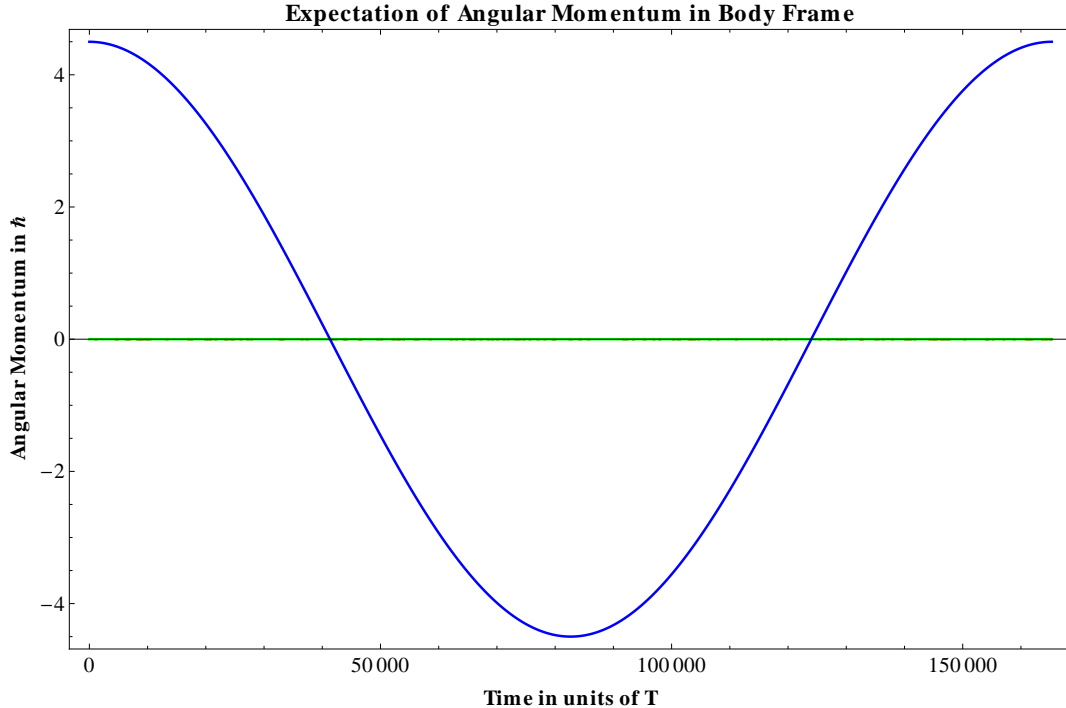


FIG. 5: Plot of $\langle \mathbf{J}(t) \rangle$ for the ground state polarized along $\hat{\mathbf{z}}$, with $\langle J_x \rangle$ in red (not visible), $\langle J_y \rangle$ in green, and $\langle J_z \rangle$ in blue.

$\langle J_z \rangle$ of the initial state becomes rapidly smaller, while $\langle J_x \rangle$ grows. We expect that at higher levels non-Abelian effects become stronger. Indeed we find that in the body frame, oscillations of the $\langle J_x \rangle$ and $\langle J_y \rangle$ components become more pronounced, which may be easier to detect. It would therefore be interesting if one can select an initial energy level, perhaps by applying a suitable a/c pulse to excite the molecule and then selecting the starting state within that level by applying a small d/c field which is gradually reduced to zero.

VII. DISCUSSION

We have derived the equations of motions of the Majorana points for states undergoing non-Abelian adiabatic evolution. We focussed primarily on the case when the degenerate subspace consists of a Karmers pair of eigenstates for a time-reversal invariant, half-integer spin system, and on time-dependence that arises from simply rotating the host molecule about a fixed axis. We have seen that even when the effective Hamiltonian is quite simple (quadratic anisotropy only) the resulting dance of the Majorana points can be quite intri-

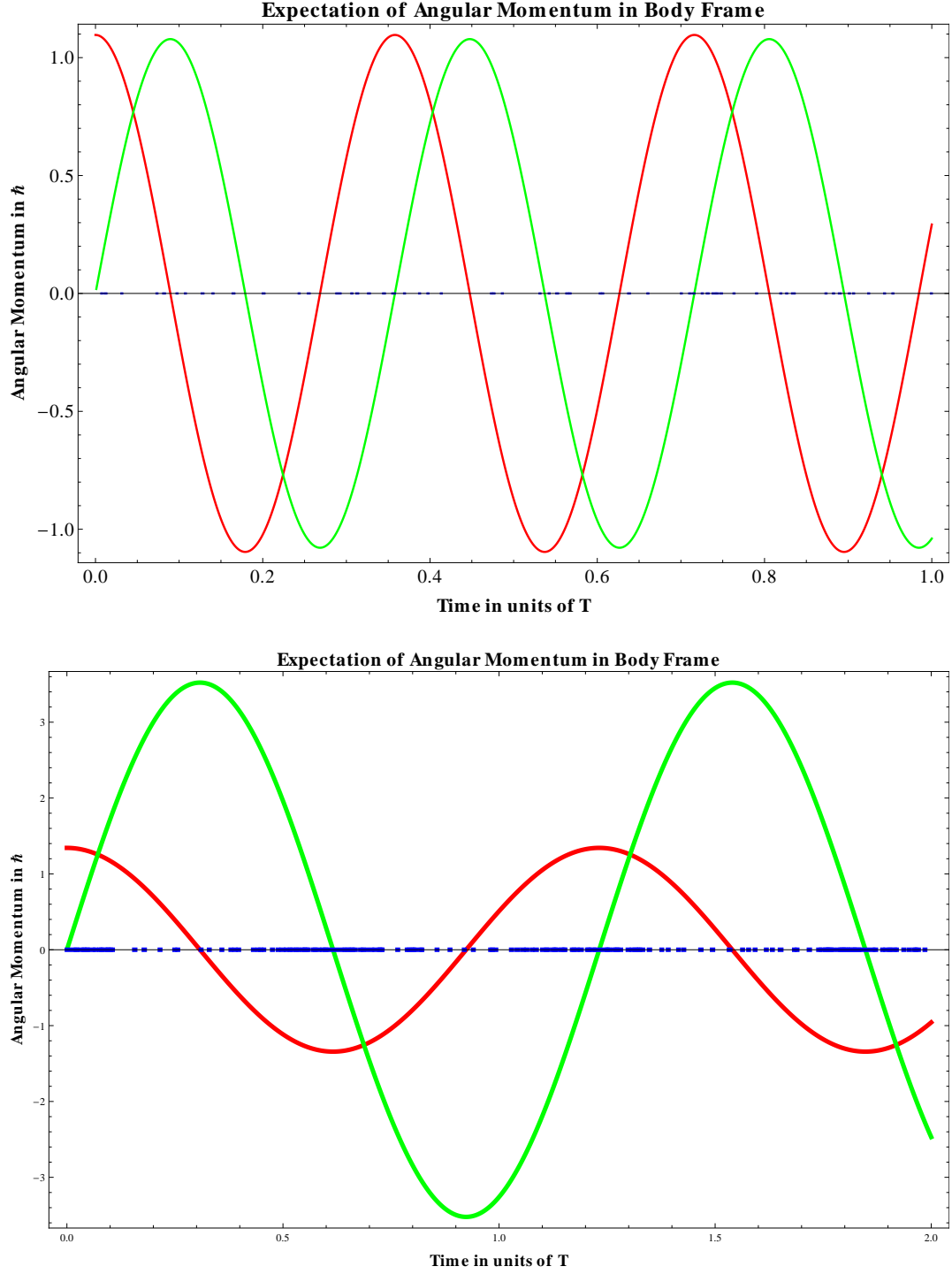


FIG. 6: Plot of $\langle \mathbf{J}(t) \rangle$ for the third (top) and fourth (bottom) excited states polarized along $\hat{\mathbf{x}}$, with $\langle J_x \rangle$ in red, $\langle J_y \rangle$ in green, and $\langle J_z \rangle$ in blue.

cate. When only one Majorana point is able to move its equation of motion is manifestly Hamiltonian. When many Majorana points are in motion the system is still Hamiltonian, but the associated symplectic form will be complicated.

Non-Abelian evolution means that the motion of the period of the Hamiltonian (the rotation period) and the period of the spin direction will in general be incommensurate. The resulting difference between the input rotation frequency and the output magnetic moment frequency can in principle be measured. A confounding effect, however, is provided by the very moment that we are trying to measure. If it is too large, the resulting magnetic field will destroy the degeneracy of the Kramers pair and will wipe out the non-Abelian dynamics. If it is too small there will be no signal indicating the spin direction. The splitting of the degeneracy means that the two not-quite degenerate states will acquire a steadily accumulating relative phase that will ultimately overwhelm the non-Abelian affect. To avoid this problem we need to have a system in which there is a substantial difference in scale between the small splitting of the near-degenerate states and the gap to the first excited state of the time-reversal invariant system. We can then spin the system fast enough that the small splitting can be neglected, while the evolution within the Kramers pair eigenspace is still adiabatic.

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